

(12) UK Patent Application (19) GB (11) 2 349 889 (13) A

(43) Date of A Publication 15.11.2000

(21) Application No 0011316.7

(22) Date of Filing 10.05.2000

(30) Priority Data

(31) 992278 (32) 11.05.1999 (33) NO

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(51) INT CL⁷

E21B 37/06 // C07C 7/152 7/20, C10L 3/10

(52) UK CL (Edition R)

C5E ECN E222

(56) Documents Cited

WO 98/23843 A1 WO 97/07320 A1 WO 96/08672 A1

(58) Field of Search

UK CL (Edition R) C5E ECN
INT CL⁷ E21B 37/06
Online: CAS ONLINE

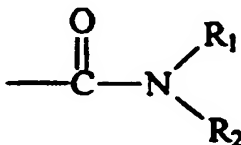
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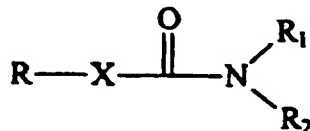
(54) Abstract Title

A method for inhibiting gas hydrate formation using polymeric amides of molecular mass less than 1000

(57) A method is provided for inhibiting the formation, agglomeration and plugging of gas hydrates in a fluid containing hydrate forming constituents. The method is particularly useful in the oil and gas industry in drilling, production and well stream transportation. The method involves adding to the hydrate forming fluids, an additive, said additive A comprising one or more amide compounds of molecular weight less than 1000 which include one or more of the following groups:



where R_1 and R_2 are independently chosen from the groups comprising of hydrogen or organic moieties having 1 - 5 carbon atoms, but the total number of the carbon atoms in R_1 and R_2 should not exceed 7, and R_1 and R_2 may be connected to each other to form a 5-7 membered ring, and may contain O, N, S, P, Si atoms in the ring, wherein the amide compounds have the following structure:



wherein R is a linear or branched alkyl or alkenyl group having 6-24 carbon atoms; R_1 , R_2 are same as above and X is a connecting group which includes one or more of the following groups: amide, ester, amine ammonium.

The additive can be used together with other components such as corrosion and scale inhibitors which do not interfere with the performance of the additive as a gas hydrate inhibitor.

A method is also provided to reduce the stability of emulsions formed from the hydrate forming fluids and additive A, by adding a second additive B, such as an aromatic, a ketone, an alcohol, a glycol an ester or a polyglycol. The preferred additive B is Butyl glycol.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1995

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Sapphire cell high pressure test equipment.

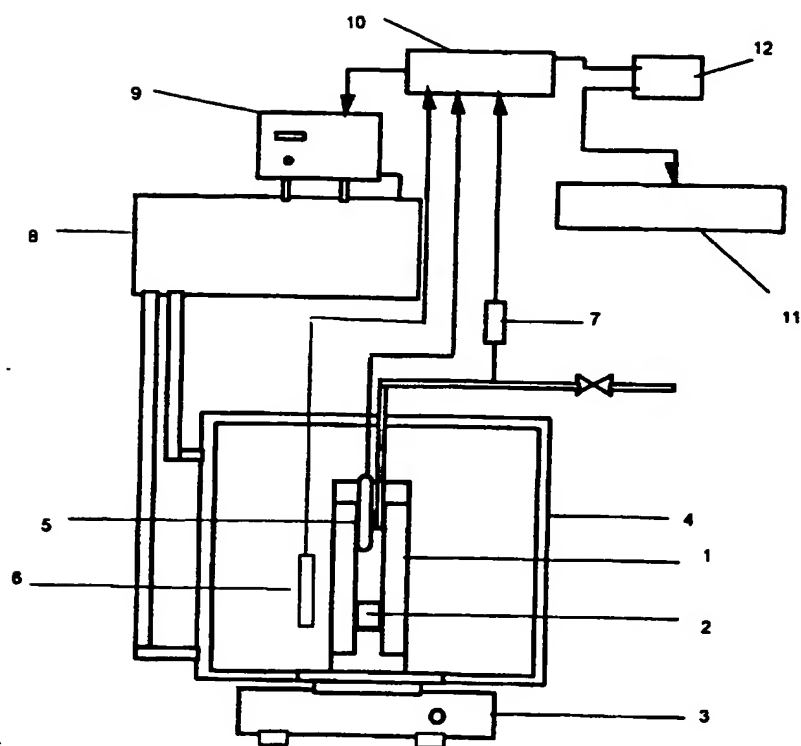


Figure 1

Field of Invention

This invention relates to a method for inhibiting the formation, agglomeration and plugging by gas hydrates of pipes containing oil and/or gas. This is relevant for both drilling and production of oil and gas.

Background of the Invention

Gas hydrates are clathrates (inclusion compounds) of small molecules in a lattice of water molecules. In the petroleum industry natural gas and petroleum fluids contain a variety of these small molecules which can form gas hydrates. They include hydrocarbons such as methane, ethane, propane, iso-butane as well as nitrogen, carbon dioxide and hydrogen sulfide. Larger hydrocarbons such as n-butane, neopentane, ethylene, cyclopentane, cyclohexane and benzene are also hydrate forming components. When these hydrate forming components are present with water at elevated pressures and reduced temperatures the mixture tends to form gas hydrate crystals. For example, ethane at a pressure of 1 MPa forms hydrates only below 4°C whereas at 3 MPa gas hydrates can only form below 14°C. These temperatures and pressures are typical operating environments where petroleum fluids are produced and transported.

If gas hydrates are allowed to form inside a pipe used to transport natural gas and/or other petroleum fluids they can eventually block the pipe. The hydrate blockage can lead to a shutdown in production and significant financial loss. The oil and gas industry uses various means to prevent the formation of hydrate blockages in pipelines. These include heating the pipe, reducing the pressure, removing the water and adding anti-freezes such as methanol and ethylene glycols which act as melting point depressants. Each of these methods is costly to implement and maintain. The most common method used today is adding anti-freezes. However, these anti-freezes have to be added at high concentrations, typically 10-40% by weight of the water present, in order to be effective. Recovery of the anti-freezes is also usually required and involves a costly procedure. Consequently, there is a need for alternate cheap methods for preventing hydrate blockages in oil and gas drilling and production.

An alternative to the above methods is to control the gas hydrate formation process using nucleation and crystal growth inhibitors and/or other chemicals that prevent the formed hydrate crystals from agglomerating. These types of chemicals are widely known and used in other industrial processes. The advantage of using these chemicals to control gas hydrate formation is that they can be used at concentrations of 0.01 to 2% which is much lower than for anti-freezes.

It is possible to design molecules which bind to hydrate surfaces in preference to the bulk water. The hydrate surface interaction of the molecule can affect the nucleation and growth rate of the hydrate as well as the morphology, aggregation and agglomeration tendencies.

It is known that water-soluble polymers with monomers such as N-vinyl pyrrolidone (Int. Patent Appl. Publ. WO 93/25798), N-vinyl caprolactam (Int. Patent Appl. Publ. WO 94/12761), N-isopropylmethacrylamide (Int. Patent Appl. Publ. WO 96/41834), and acryloylpyrrolidine (Int. Patent Appl. Publ. WO 96/08672) are able to slow down the nucleation and growth of gas hydrates. These polymers have a limited performance range. For example, they are not applicable for situations where the driving force for hydrate formation is high such as during and after shut-in of a subsea multiphase pipeline at high pressure and low seabed temperature. The driving force is often described as the subcooling in the system, i.e. the difference between the temperature of the system and the equilibrium temperature for hydrate formation at the system pressure. A more accurate description is the potential of the system to form gas hydrates. At very high driving forces, the prevention of rapid hydrate formation by these water-soluble polymers is not possible. Secondly, once rapid hydrate formation takes place the hydrate agglomerates and deposits causing a plug. Hence, a different technique is required to prevent hydrates from plugging. This technique uses amphiphilic compounds with polar head groups which interact with hydrate surfaces, as per the side chain groups in the water-soluble polymers, but the polar head groups are now connected directly or indirectly to a longer hydrophobic chain. In US Patent 5,460,728 and Int. Patent Appl. Publication WO 95/17579 the use of alkylated ammonium, phosphonium and sulphonium compounds is disclosed, wherein the alkylated groups have 4 or more carbon atoms. These compounds have high toxicities to marine organisms, as well as being poorly biodegradable. The environmental impact of these

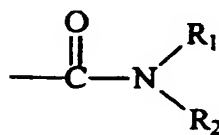
additives will restrict their use in offshore oil and gas operations. In EP 323307A, the use of amphiphilic additives to prevent hydrate agglomeration is claimed. The additive examples given prevent agglomeration via formation of very stable water-in-oil emulsions. These emulsions are costly to separate at the produced fluid process facilities. Further, condensed water formed during shut-in conditions of a pipeline will not be emulsified and can be converted to hydrate which can plug the line. In EP 323774, non-ionic amphiphilic additives from the group consisting of esters of polyols and substituted or unsubstituted carboxylic acids is claimed. Again, the additive examples given prevent agglomeration via formation of very stable water-in-oil emulsions. In EP 323775, non-ionic amphiphilic additives from the group consisting of amide compounds is claimed. Again, the additive examples given prevent agglomeration via formation of very stable water-in-oil emulsions.

It is an object of this invention to provide a method of controlling gas hydrate formation and plugging using additives added at low concentrations to a gas hydrate forming fluid.

The present inventors have surprisingly found a method for inhibiting the formation and agglomeration of gas hydrates in pipelines being exposed to hydrate forming conditions. This new method includes the use of a group of amide compounds which will be further disclosed in the following. The method of the invention utilizing said amide compounds for the prevention of hydrate formation and agglomeration as discussed above, obviates the insufficiencies of the prior art discussed above.

Summary of Invention

It has surprisingly been found that amide additives A containing one or more of the following groups:



where R_1 and R_2 are independently selected among the groups comprising of hydrogen or organic moieties having 1 - 5 carbon atoms, but the total number of the carbon atoms in R_1 and R_2 should not exceed 7, and R_1 and R_2 may be connected to each other to form a 5-7 membered ring, which may include O, N, S, P, Si atoms in the ring, inhibit the

growth, agglomeration and deposition of gas hydrates when added at low concentration to a hydrate forming system containing hydrocarbons and water.

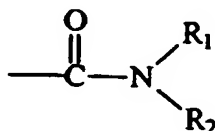
In structure A, R is an linear or branched, alkyl or alkenyl group having 6 - 24 carbons atoms. R₁ and R₂ are independently chosen from the groups comprising of hydrogen or organic moiety having 1 - 5 carbon atoms, but the total number of the carbon atoms in R₁ and R₂ should not exceed to 7, and R₁ and R₂ may be connected each other to form 5 - 7 membered ring, and may be containing O, N, S, P, Si atoms in the ring. X is a direct bond or a connecting group.

Additives A are able to interact primarily via the alkylamide head group or groups with the surfaces of hydrate crystals thereby interfering with the growth process of the hydrate crystals. The group R prevents agglomeration of hydrate crystals by making the surface hydrophobic. The additives A will also adhere to some extent to pipe walls thereby reducing the adhesion of hydrate crystals to the pipe walls. The amphiphilic nature of the additives A is such that they concentrate at the water-hydrocarbon interfaces where hydrate formation is most prominent.

During shut-in situations (i.e. when the hydrate forming fluids are static), the fluids often separate out into free water, emulsion and liquid hydrocarbon layers. We have found that hydrate formation usually takes place most prevalently in the emulsion layer, i.e. where there is a large area of water-oil interface. If the emulsion layer is large and the shut-in time is long under hydrate forming conditions, considerable solid hydrate can be formed during the shut-in. It is easier to restart the line if little or no solid hydrate is present in the line. Therefore, it is preferable to prevent emulsions from existing during the static shut-in period in order to reduce the amount of hydrate formation during the static shut-in period. It is an invention of this patent that one of more additives B can be added to the additive A, to reduce the emulsion stability during static (shut-in) situations. Preferably, these additives B are fatty acid esters, glycol esters, as well as alcohols, glycols or polyglycols, and ketones (e.g. methyl butyl ketone, and aromatics in general (such as toluene and xylene). An example is butyl glycol also known as butyl cellosolve.

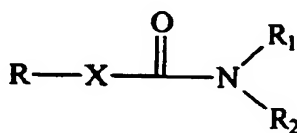
Detailed Description of the Invention

The present invention relates to a method for inhibiting and/or retarding clathrate hydrate formation and/or agglomeration by adding an additive A to a system capable of forming clathrate hydrate, said additive comprising amide compounds of a molecular weight of less than 1000 including one or more of the following groups:



where R_1 and R_2 are independently chosen from the groups comprising hydrogen or organic moieties having 1 - 5 carbon atoms, but the total number of the carbon atoms in R_1 and R_2 should not exceed 7, and R_1 and R_2 may be connected to each other to form a 5-7 membered ring, which may include O, N, S, P, Si atoms.

Further, such compounds may have the structure



where R is a linear or branched, alkyl or alkenyl group having 6 - 24 carbons atoms, R_1 and R_2 are independently chosen from the groups comprising of hydrogen or organic moiety having 1 - 5 carbon atoms, but the total number of the carbon atoms in R_1 and R_2 should not exceed 7, and R_1 and R_2 may be connected to each other to form a 5-7 membered ring, and may contain O, N, S, P, Si atoms in the ring, and X is a direct bond or a connecting group including one or more of the following groups, amides, esters (including fatty acid esters and glycol esters), amines or ammonium.

The additives A are able to interact primarily via the alkylamide head group or groups with the surfaces of hydrate crystals thereby interfering with the growth process of the hydrate crystals. The group R prevents agglomeration of hydrate crystals by making the surface hydrophobic. The additives A will also adhere to some extent to pipe walls thereby reducing the adhesion of hydrate crystals to the pipe walls. The amphiphilic

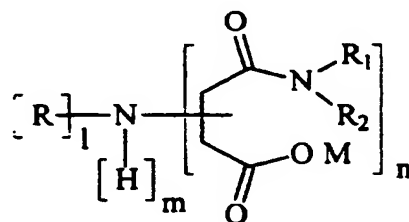
nature of the additives A is such that they concentrate at the water-hydrocarbon interfaces where hydrate formation is most prominent.

Preferably these compounds have a molecular weight less than 1000.

Further, their connecting group X of these compounds may include a second polar
5 terminal group.

Preferred groups R_1 and R_2 are R_1 = isopropyl, R_2 = H; R_1 = isobutyl, R_2 = H; R_1 = ethyl, R_2 = ethyl; R_1 and R_2 = tetramethylene to form a 5-membered pyrrolidino ring with a nitrogen atom.

The additives A can have one or more alkylamide terminal groups. Two or more such
10 alkylamide terminal groups can provide a stronger interaction with the hydrates surfaces than one such group. For example, one embodiment of the invention is a method using a preferred class of additives A having the following structure:



where $l = 1$ or 2 ;

15 $m = 0$ or 1 ;

$n = 1$ or 2 ;

$l+m+n = 3$

and $M = \text{H}$, a metal atom, ammonia or a primary, secondary or tertiary organic amine.

The groups R can be different when $l = 2$, and further, the first R_1 and R_2 may be
20 different from the second R_1 and R_2 when $n=2$.

Another preferred method uses the amide compounds having the following structure:

§

$$\left[\text{R} \right]_1 - \text{N} \left[\begin{array}{c} \text{Y} - \text{C}(=\text{O}) - \text{N} \begin{array}{l} \text{R}_1 \\ \text{R}_2 \end{array} \\ \text{H} \end{array} \right]_m \left. \right]_n$$

10 $m = 0$ or 1 ;

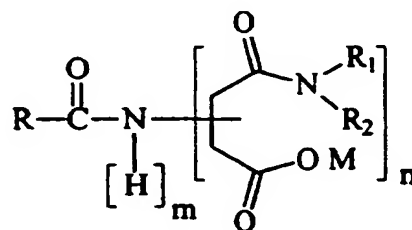
$$l+m+n = 3$$

¹⁵ groups CONR_1R_2 may be mutually different when $n=2$.

$$\begin{array}{c}
 \text{O} \\
 || \\
 \text{R}-\text{N}-\text{Y}-\text{C}-\text{N}-\text{R}_1 \\
 | \quad \quad | \\
 \text{Z}-\text{C}-\text{O M} \\
 || \\
 \text{O}
 \end{array}$$

where Y and Z are the same or different connecting groups selected from alkylene, preferably C₁-C₄ alkylene, and R, R₁, R₂ and M are as defined above.

Another preferred method uses a class of additives A having the following structure:



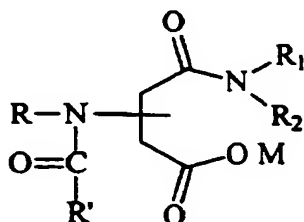
5 where $m = 0$ or 1 ;

$n = 1$ or 2 ;

$m+n = 2$

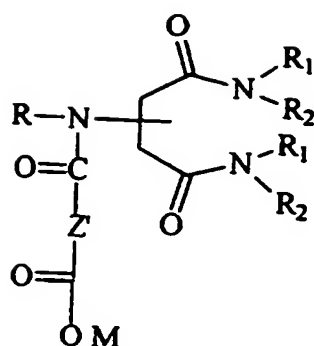
and $M = \text{H}$, a metal atom, ammonia or a primary, secondary or tertiary organic amine,
and R, R₁ and R₂ have the meanings defined above. When $n=2$ the first meaning of
10 the group CONR_1R_2 may be different from the second meaning of this group.

Another preferred method uses the class of additives A having the following structure:



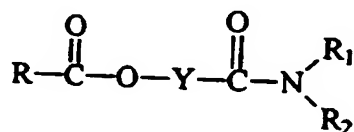
where R is a linear or branched, alkyl or alkenyl group having 6 - 24 carbons atoms, R'
is a linear or branched, alkyl or alkenyl group having 1 - 24 carbons atoms, and $M = \text{H}$,
15 a metal atom, ammonia or a primary, secondary or tertiary organic amine.

Another preferred method uses the class of additives A having the following structure:

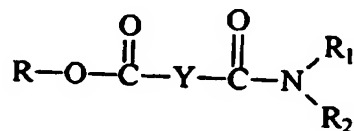


where Z' is a connecting group selected from alkylene, and $M = H$, a metal atom, ammonia or a primary, secondary or tertiary organic amine, and R , R_1 and R_2 have the meanings defined above.

- 5 Another preferred method uses the class of additives A having the following structure:

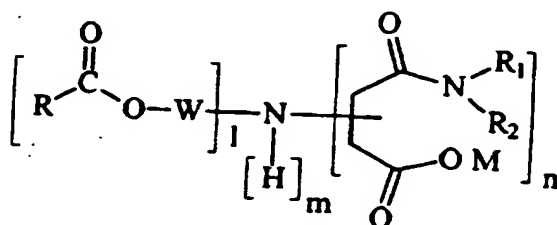


or the structure:



10 where Y is a connecting group selected from alkylene, alkyleneoxy, and polyalkyleneoxy.

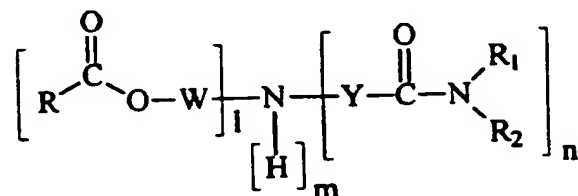
Further, a preferred method uses the compounds of the formula



where W is a connecting group selected from alkylene, alkyleneoxy, polyalkyleneoxy, and R , R_1 , R_2 , M , l , m , and n are as defined above. The first R and W can be different

from the second R and W when $l=2$. Also, the first R_1 and R_2 may be different from the second R_1 and R_2 when $n=2$.

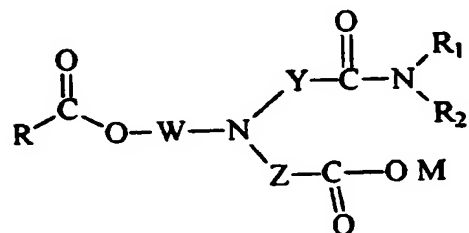
Another preferred method uses the amide compounds having the following structure:



5

where W, R, R_1 , R_2 , Y, l, m, and n are as defined above. The first R and W can be different from the second R and W when $l=2$. Also, the first CONR_1R_2 may be different from the second CONR_1R_2 when $n=2$.

10 Another preferred method uses the amide compounds having the following structure:



wherein W, Y, M, R, R_1 , and R_2 have the meanings defined above, and Z is a connecting group selected from alkenes, preferable a C_1 - C_4 alkylene.

15 Suitably between 0.05 and 10 wt. %, based on the water content, of the additive is added to the water/hydrocarbon mixture.

Particularly between 0.1 and 0.8 wt. %, based on the water content, of the additive is added to the water/hydrocarbon mixture.

Suitably a corrosion inhibitor is added to the water/hydrocarbon mixture.

Suitably also a polymer of an ethylenically unsaturated N-heterocyclic carbonyl compound is added to the hydrocarbon water mixture.

Particularly the polymer is a polymer or copolymer of vinyl caprolactam or vinyl pyrrolidone.

- 5 Preferably a N-alkyl or N,N-dialkyl acrylamide polymer is added to the hydrocarbon/water mixture.

Further the polymer can be a polymer or copolymer of acryloylpyrrolidine or N-isopropylacrylamide.

- 10 Suitably a polymer with a heteroatom backbone and sidechains containing amide groups is added to the hydrocarbon water mixture.

Preferably the polymer is a copolymer derived from a comonomer with 6-30 carbon atoms.

Particularly the comonomer is an alkyl acrylate or a unsaturated hydrocarbon.

Suitably a salt is also added to the hydrocarbon/water mixture.

- 15 Preferably the salt is sodium chloride.

Suitably the products added to the hydrocarbon/water mixture also contain an aromatic, ketone, ester (including fatty acid esters and glycol esters), alcohol or glycol solvent.

Preferably R_1 and R_2 of the amide group defined above are chosen from the groups ethyl, isopropyl, tetramethylene and isobutyl.

- 20 Suitably one or more second additives is used together with the first additive to reduce the formation and stability of emulsions in the hydrate forming fluids.

Preferably the second additive is an alcohol, glycol or polyglycol.

Further the second additive may be an ester (including fatty acid esters and glycol esters).

- 25 Particularly the second additive is butyl glycol.

One or more of the preferred additives can be used in combination. For example two or more additives with different groups R, or two or more additives with different groups R₁ and R₂.

The total amount of additives A of this invention that has to be added is generally between 0.05 and 5 wt. %, preferably between 0.1 and 0.5 wt. %, based on the amount of water in the hydrocarbon-containing mixture. The products can be added to a stream of light hydrocarbons and water either as powders or preferably in concentrated solution.

One or more additives B can be added to the additive A, to reduce the emulsion stability during static (shut-in) situations. Preferably, these additives B are fatty acid esters, alcohols, glycols or polyglycols. An example is butyl glycol, also known as butyl cellosolve. The concentration of such additives to be added is between 0.0001 to 2 wt.% based on the amount of water in the hydrocarbon-containing mixture. Additive B can also act as a solvent for additive A.

The additives A, or mixtures of additives A and B can be used together with other surfactants and polymers which inhibit the nucleation and crystal growth of gas hydrates. This is useful to reduce the amount of solid hydrate in the line, firstly since it is easier to handle liquid transport, secondly it makes it possible to use additives A at a higher water cut (% of water compared to total liquids) than using additives A alone.

Preferred surfactants include alkylpyrrolidones. Preferred polymers include homopolymers, copolymers and terpolymers derived from vinyl pyrrolidone, vinyl caprolactam, amide derivatives of maleic anhydride, isopropylacrylamide and acryoylpyrrolidine. Specific polymers include polyvinylpyrrolidone, polyvinylcaprolactam, vinylpyrrolidone:vinylcaprolactam copolymer and vinyl caprolactam:vinyl methyl acetamide copolymer.

The mixture of compounds of this invention can be used together with one or more of the following additives:

- a corrosion inhibitor. This additive is preferably added to an amount of between 0.01 and 0.5 wt. % based on the water content. This additive can have a beneficial effect

on forming a hydrophobic coating at the pipe wall thereby reducing the adherence tendencies of the hydrate.

• an material containing an alkylammonium quaternary group where at least one of the alkyl groups on the quaternary nitrogen atom has 4-5 carbon atoms. Examples include tetrabutylammonium salts and tetrapentylammonium salts and compounds, surfactants and polymers containing the dipentyl-, dibutyl-, tripentyl- and tributyl ammonium quaternary group. These additives are also preferably added to an amount of between 0.01 and 0.5 wt. % based on the water content.

• a material containing an alkylamine oxide group where at least one of the alkyl groups on the nitrogen atom of the amine oxide has 4-5 carbon atoms. Examples include tributylamine oxide and tripentylamine oxide. These additives are also preferably added to an amount of between 0.01 and 0.5 wt. % based on the water content.

• A solvent. Examples are ester based solvents, alcohols, ketones, glycols or polyglycols. Examples include isopropanol, 1-butanol, 2-butanol, butoxyethanol, 2-butoxypropan-2-ol, and methyl butyl ketone. The solvent is preferably added to an amount of between 0.05 and 2.0 wt. % based on the water content.

• A salt. Preferably a halide salt. Examples include sodium chloride and calcium chloride. The salt is preferably added at an amount of between 0.05 and 5.0 wt. % based on the water content.

A preferred method includes compounds as defined above having a molecular weight less than 1000.

The present invention also relates to the use of the compounds discussed above in connection with the methods of inhibiting gas hydrate formation and agglomeration.

The present invention further relates to the use of the additives A and B discussed above to reduce the emulsion stability of fluids capable of forming emulsions and hydrates.

The following examples are provided to elucidate the invention.

These examples must in no way be considered as limiting the scope of the invention to the examples presented. The scope of the invention is defined in the patent claims.

Examples

Equipment and test procedure

To evaluate the performance of the additives of this invention, the examples given herein use high pressure sapphire cells and methods of using them described in M.A.

- 5 Kelland, T.M. Svartaas and L.A. Dybvik, Proc. SPE Annual Technical Conference/Production Operations and Engineering, 1994, pp 431-438.

Sapphire cell high pressure test equipment

The sapphire cell high pressure test equipment is illustrated in figure 1.

- 10 The sapphire cell was mounted in a cooling bath. The sapphire cell consists of a sapphire tube 1 enclosed in a holder between two stainless steel end pieces. The cell has an inner diameter of 20 mm, height 100 mm and a wall thickness of 20mm. 15 mm of the top piece and 13 mm of the bottom piece protrudes into the cell, and the total volume between the top and bottom piece is 22.8 ml. The sapphire cell is equipped with a stirrer mechanism. A stirrer blade 2 is connected to a magnet house in the bottom end
- 15 piece via an axle. An outer rotating magnetic field 3 created by a laboratory stirrer bar drive is used to regulate the stirrer speed. The stirrer motor can be regulated to maintain a constant speed (independent of motor load) in the range 0 to 1700 rpm. The regulator/amplifier unit has output connections for both torque and rotation speed readings. The stirrer speed readings are calibrated using a stroboscope.

- 20 The sapphire cell is placed inside separate double-walled, transparent carbonate plastic cylinders with four separate windows at 0, 90, 180, 270° for visual observations. Temperature control of the cell is obtained by circulating water in the plastic cylinders and through a cooler/heater unit 8 connected to a temperature control unit 9. The cell system is equipped with two temperature sensors for the measurement of the
- 25 temperature inside the cell 5 (in the gas phase) and in the water bath 6. Pressure is measured with a pressure transducer 7 through the inlet tubing connection in the top end piece of the cell. The temperature was measured to an accuracy of $\pm 0.1^\circ\text{C}$ and the pressure was measured with an accuracy of ± 0.2 bars. Video recordings of the experiments were also made. All data were assembled in a data logger 10. The data

could be taken out on a printer/plotter 11. A computer 12 with monitor screen transfers the data from the data logger 10 to the printer/plotter 11.

The same procedure for preparation of the experiment and filling of the cell was followed in all experiments. All tests were performed using fresh synthetic sea water (SSW = 3.6%), synthetic natural gas (SNG) and a clear condensate from a North Sea field. The water cut was usually 18-25% in all cell experiments.

A description of the general test procedure is given here:

- 1) The additive to be tested was preferably dissolved or dispersed in Synthetic Sea Water (SSW) to the desired concentration. If it could not be dissolved or dispersed, it was used as a neat product added directly to the cell.
- 2) The magnet housing of the cell was filled with the aqueous solution containing the additive to be tested. The magnet housing was then mounted in the bottom end piece of the cell, which thereafter was attached to the sapphire tube and the cell holder.
- 3) The desired amount of the aqueous solution, which preferably contains dissolved or dispersed additive, was filled in the cell (above the cell bottom) using a pipette, the top end piece was mounted, and the cell was placed into the cooling bath (plastic cylinder).
- 4) The temperature of the cooling bath was adjusted to 2-3°C outside the hydrate region at the pressure conditions to be used in the experiment.
- 5) Prior to loading the cell with recombined SNG/condensate it was purged two times with the SNG used in the experimental hydrocarbon fluid.
- 6) The data logging and video recording were started, and the cell was loaded with the hydrocarbon fluid to the desired pressure while stirring at 700 rpm. The hydrocarbon fluid was a recombined fluid made up of SNG and condensate. When the temperature and pressure in the cell had stabilised the stirring was stopped. The equipment was thus ready for testing the additives.

Once the cell is prepared as described above, two test procedures are usually carried out. The first procedure is to start stirring at 700 rpm with simultaneous cooling of the cell down to a set temperature within the hydrate forming region for the given system. The standard set temperature used was ca. 4°C. Using this procedure, we find that hydrates

begin to form at a range of temperatures dependent mainly on the hydrate inhibition properties of the additive and the statistical variations in the system which are related to the equipment and test procedure.

The second procedure is to cool the fluids to the minimum temperature without stirring.

5 The standard set temperature used was ca. 4°C. The cooling time is usually 1-2 hours. Then when the temperature is stable, the stirring is started. Using this second procedure we have found that detectable amounts of hydrates are rarely observed during the 1-2 hours of cooling without stirring, rather they are first detected after stirring is started

We have also found the performance of additives designed to inhibit growth,
10 agglomeration and deposition of gas hydrates is dependent on the driving force for hydrate formation in the system. Therefore, the second test procedure is a more severe test for the additive since when stirring is started the driving force is at a maximum. In the first procedure, hydrates can form at higher temperatures than the maximum temperature, i.e. at lower driving forces.

15

Experiments

1. Performance of Additives A in preventing hydrate agglomeration and deposition

The experiments described herein, were conducted at constant temperature. Thus, once the temperature and pressure had stabilised after loading of the cell the stirring was
20 stopped. The closed cell was then cooled down to the experimental temperature, resulting in a decrease in pressure to a value P_0 . When the temperature and pressure again had stabilised, stirring at 700 rpm was started.

The results of all experiments were recorded by plotting temperature, pressure (or the Total Gas Consumption TGC) and torque as a function of time. The examples are given
25 in Table 1. The experiments were carried out at various initial pressures P_0 and at constant temperatures in the range 3.6-4.1°C. An experimental temperature of 4.0°C and 90 bar was equivalent to a subcooling of ca. 14.7°C. An experimental temperature of 4.0°C and 200 bar was equivalent to a subcooling of ca. 18°C.

The water cut was in the range ca. 15-20%. The condensate was from the Frigg field (North Sea) but different condensate samples (7-9) were used as indicated in the table. The aqueous phase was synthetic sea water with 3.6 wt.% salts except for experiments with an asterisk (*) next to the experiment number in which a 0.5 wt.% solution was used. dTGC is the amount of gas uptake (in bars) due to hydrate formation. "After S-u" refers to the average/maximum torque measurement after start-up and during the first 2.5 hours of stirring. The "stable level" is the average/maximum of the torque measurement after 2.5 hours after the start of stirring. Experiments were terminated ca. 16-20 hours after start of stirring.

- 10 A good additive forms a slurry of hydrates which does not agglomerate or deposit in the equipment and does not give any significant increase torque throughout the experiment. However, some increase in torque is inevitable due to the higher viscosity of the hydrate slurry compared to the water/hydrocarbon mixture. Some times loose particles deposit on the walls above the level of the stirred liquid. These can sometimes be washed off by
15 increasing the stirrer rate for a short period.

The grading codes A-E are used to evaluate the overall relative performance of the additives. Experiments with codes A-D are all inside the claims of the invention since they give an improved result on the experiment with no additive. Code E represents fast plugging of the cell and is outside the claims of the invention.

- 20 The codes in the last 3 columns of Table 1 refer to the following observations:

Lp: Loose particles

wo: washed off by 1300rpm stirring

Fw: hydrate film on sapphire wall

A: agglomerates

- 25 Dwnwo: deposits on sapphire wall, not washed off by 1300rpm stirring

Dw: deposits on sapphire wall

Dst: deposits on stirrer blade

hDw: hard deposits on sapphire wall

Vs: viscous slurry

prs: hydrate particles residues on stirrer blade

Db: deposits at bottom of sapphire cell

pf: hydrate particle film residues

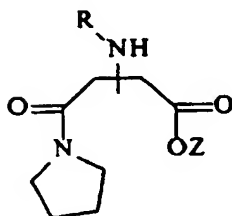
5 f: hydrate film residues

Spr-s: stirring problems, stirrer stopped

+: more

-: less

10 The samples codes in the table refer to the following structures:



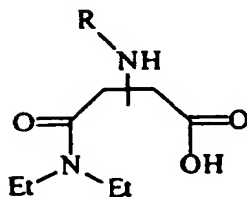
OTMAA (Z = H, R = C₈H₁₇)

n-OTMAA (Z = Na, R = C₈H₁₇)

NTMAA (Z = H, R = C₉H₁₉)

DTMAA (Z = H, R = C₁₀H₂₁)

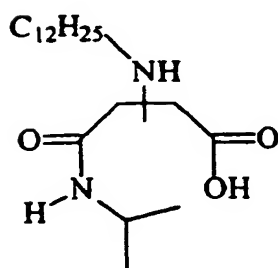
LTMAA (Z = H, R = C₁₂H₂₅)



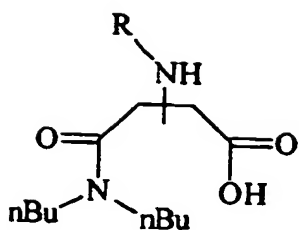
FX-ODEAA (R = C₈H₁₇)

FX-DDEAA (R = C₁₀H₂₁)

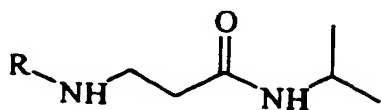
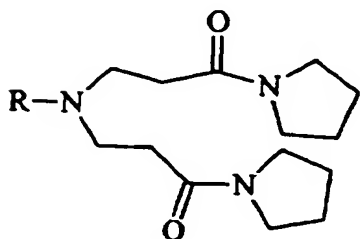
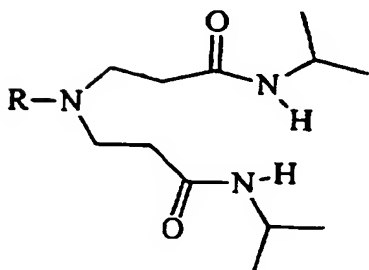
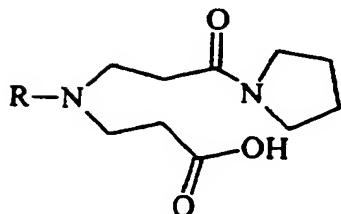
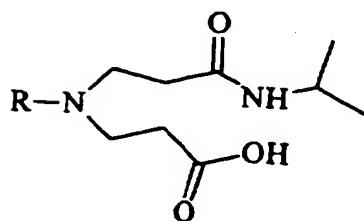
FX-LDEAA (R = C₁₂H₂₅)

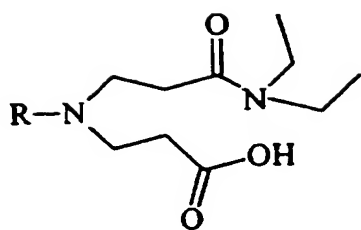
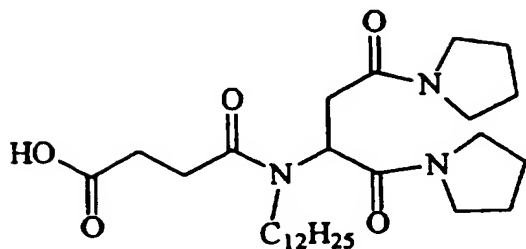


FX-LIPAA

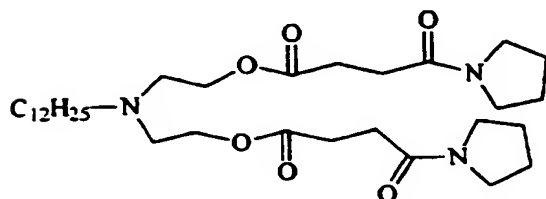


FX-LDBAA

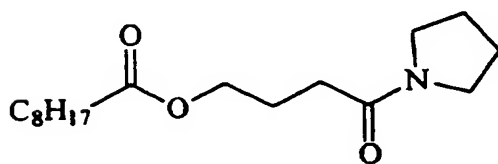
FX-AIP8 ($R = C_8H_{17}$)FX-AIP12 ($R = C_{12}H_{25}$)FX-AIP18 ($R = C_{18}H_{37}$)FX-DPCEOA ($R = C_8H_{17}$)FX-DPCEDA ($R = C_{12}H_{25}$)FX-DIPCECA ($RNH_2 = \text{coconut amine}$)FX-ACAA-TMO ($R = C_8H_{17}$)FX-ACAA-TMD ($R = C_{12}H_{25}$)FX-ACAA-IPO ($R = C_8H_{17}$)FX-ACAA-IPD ($R = C_{12}H_{25}$)

FX-ACAA-DEO ($R = C_8H_{17}$)FX-ACAA-DED ($R = C_{12}H_{25}$)

FX-TMD-TMPA



FX-LDEDPS



FX-PCPN

The materials are either commercially available, as indicated, or can be prepared by standard synthetic procedures familiar to those skilled in the art.

Table 1: Examples

Expt. No.	Chemical Code	Conc. (ppm)	Frigg #	Water	Po	To	ΔT (°C)	Grade	After S-u (mNm)	Stable level (mNm)	Very late (mNm)
1	no additive							E	Plug within 2-10min.		
2	OTMAA	5000	8	21,9	122,55	4,10	15,74	A	3.4 / 5.9	3.2 / 5.4	Lpwopr
3	Na-OTMAA	10 000	8	16,0	ca. 200	4,11	ca. 18	A	2.7 / 3.5	3.6 / 9.7	Lpwo
4	NTMAA	5000	9	19,9	91,87	3,70	13,89	A	3.5 / 6.8	3.3 / 5.5	Lp-wo
5	DTMAA	5000	9	17,3	92,21	3,61	14,00	A	3.3 / 5.9	3.3 / 7.2	Lpwo
6	LTMAA	5000	9	20,5	92,10	3,71	13,89	B	3.9 / 6.6	3.2 / 5.7	Lpwo, Fw
7	OTMAA+LT MAA	5k+5k	8	18,2	200,11	4,12	18,02	A	4.9 / 14.5	5.8 / 8.2	Lpwof-
8	ODEAA	5000	9	19,1	91,71	3,70	13,88	D	A, Dst, Lpw	A, Dst, Lpw	
9	DDEAA	5000	9	20,4	91,78	3,70	13,89	A	3.3 / 6.4	3.2 / 6.7	Lpwo
10	LDEAA	5000	8	19,5	123,25	4,10	15,77	A	3.3 / 5.6	3.4 / 5.8	Lp-wo
11	LIPAA	5000	9	19,0	92,22	3,71	13,90	D	12.3 / 27.2	13.1 / 28.2	A, Dwnwo
12	LDBAA	5000	9	16,7	91,72	3,71	13,87	D	A, Dw		A, Dw
13	AIP8 + AIP12 + AIP18 75:20:5	5000	7	18,1	95,24	4,17	13,77	A	3.6 / 5.5	3.6 - 4.7	Lpwo, Fw-

14	DPCEOA	5000	9	19,8	91,72	3,70	13,88	D	4.4 / 8.1	4.1 / 9.0	A, Dst
15	DPCEDA	5000	8	21,0	122,14	4,11	15,72	A	3.5 / 6.6	3.4 / 8.9	Lpwo
16 *	DPCEDA	5000	9	19,4	91,71	3,71	14,90	A	4.4 / 6.7	3.5 / 6.2	Lpwo
17	DIPCECA	5000	9	19	ca. 90	3,7	14	A	4/5	4/5	Lpwo
18	DIPCECA + butyl glycol	5000	9	15,3	123,03	4,17	14,18	B	3.7/11,0	3.5/9,5	Lpwo
19	ACAA-TMO	5000	9	18,9	91,78	3,71	13,88	D	4.7 / 8.8	3.9 / 7.5	A, hDw
20	ACAA-TMD	5000	9	18,5	91,49	3,70	13,87	A	3.4 / 5.9	3.3 / 6.8	Lpwo
21 *	ACAA-TMD	5000	9	18,9	91,87	3,61	15,00	C	9.1/16.5	4.2/14.1	
22	ACAA-IPO	5000	9	18,2	91,71	3,71	13,87	C	3.8 / 6.2	3.9 / 6.9	Lptwo
23	ACAA-IPD	5000	9	20,5	91,66	3,60	13,98	A	3.7 / 6.4	3.5 / 6.4	Lpwo
24 *	ACAA-IPD	5000	9	20,6	92,12	3,61	15,00	C	4.7 / 8.8	5.2 / 11.7	Lpwo, Dst
25	ACAA-DEO	5000	9	18,9	92,32	3,70	13,91	D	11.1 / 27.5	10.9 / 25.2	A, Dst
26	ACAA-DED	5000	9	18,9	92,26	3,70	13,91	D	3.6 / 8.4	4.0 / 7.6	Vs, Dst
27	TMD-TMPA	5000	9	18,9	91,90	3,70	13,89	C	4.0 / 9.1	3.9 / 8.3	Lpwo
28	LDEDPS	5000	9	21,3	91,58	3,69	13,89	D	6.0 / 12.1	5.3 / 15.2	Vs, Dst
29	PCPN	5000	9	20,9	91,78	3,70	13,89	D	8.5 / 24.6	8.5 / 18.4	A, Dw, Dst

2. Emulsion Stability Tests with Additives A and B

Experiments were conducted in the same sapphire cell equipment described earlier.

It was important to test the emulsion stability using the gas components, and not just the hydrocarbons which are liquid at room temperature. This was because the gas components are liquid or dissolve in the liquid hydrocarbon under pressure and thus affect the emulsion stability.

The test procedure was as follows. 3.2g of water was added to the cell in all experiments. Additives A were added to the cell at 5000 ppm based on the water phase. The cell was pressurised to ca. 120 bar at room temperature using a natural gas blend as used in the performance tests. The height of the water and liquid hydrocarbon phases was measured. The fluids in the cell were stirred for 30 minutes at 20°C. Stirring was stopped and the time for complete break of the emulsion into water and liquid hydrocarbon phases was measured. Experiments were repeated with blends of Additives A and B. The results are given in Table 2.

Table 2: Emulsion breaking times

Additive A	Additive B	Concn (ppm)	Pressure (bar)	Water (mm)	oil phase (mm)	Emulsion Break Time (sec)
ACAA-IPD	none	-	120,3	28	107	360
DIPCECA	none	-	120,5	25	108	150
ACAA-IPD	Butyl Cellosolve	10,000	120,4	26	107	260
ACAA-IPD	iso-Butyl methyl ketone	10,000	120,0	27	107	360
ACAA-IPD	Dowanol PnB	10,000	120,1	26	108	300
DIPCECA	Butyl Cellosolve	10,000	120,1	25	108	45

The results show that addition of butyl cellosolve improved the rate at which the emulsions broke when added to Additives ACAA-IPD and DIPCECA.

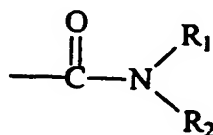
The results achieved in the hydrate formation tests and in the emulsion stability tests with the additives A and B performed as disclosed above, were not to be expected in

view of the prior art discussed in the introduction of this application. Particularly the method of the present invention enables the use of chemical compounds at low concentrations to inhibit gas hydrate formation and agglomeration in a fluid containing hydrate forming constituents, which hydrates tend to agglomerate and plug pipelines of gas and oil transport exposed to high pressures and low temperatures.

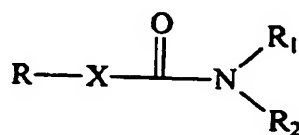
The scope of the present invention is expressed in the following claims which are also intended to comprise all equivalents obvious to those skilled in the art.

Claims

1. A method for inhibiting and/or retarding clathrate hydrate formation and/or agglomeration, characterized by adding an additive to a system capable of forming clathrate hydrates, said additive comprising amide compounds of molecular weight less than 1000 including one or more of the following groups:



where R_1 and R_2 are independently chosen from the groups comprising hydrogen or organic moieties having 1 - 5 carbon atoms, but the total number of the carbon atoms in R_1 and R_2 should not exceed 7, and R_1 and R_2 may be connected to each other to form a 5-7 membered ring, which may include O, N, S, P, Si atoms, wherein the amide compounds have the following structure



where R is an linear or branched, alkyl or alkenyl group having 6 - 24 carbons atoms,

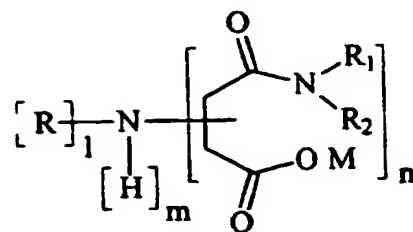
R_1 and R_2 are the same as above, and X is a connecting group including one or more of the following groups, amide, ester, amine or ammonium.

2. The method of Claim 1, characterized in that the connecting group X has at least one pendant group, and the pendant group has a polar terminal group.
3. The method of Claim 2, characterized in that the polar terminal group is a carboxyl group having the formula



wherein M is a hydrogen atom, a metal atom, ammonium group or primary, secondary or tertiary amine group.

4. The method of Claim 1, characterized in that the amide compounds have the following structure:



where $l = 1$ or 2 ;

$m = 0$ or 1 ;

$n = 1$ or 2 ;

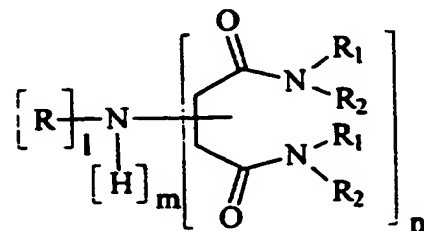
$l+m+n = 3$

and $M = \text{H}$, a metal atom, ammonia or a primary, secondary or tertiary organic amine,

R_1 and R_2 are as defined above, and further, the first R_1 and R_2 may be different from the second R_1 and R_2 when $n=2$,

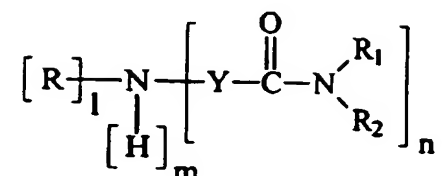
the groups R are as defined above, and can be different when $l = 2$.

5. The method of Claim 1, characterized in that the amide compounds have the following structure:



wherein l , m , and n are as defined in Claim 4 and R , R_1 and R_2 are as defined above, whereby the first R can be different from the second R when $l=2$, and further the first R_1 and R_2 may be different from the second R_1 and R_2 when $n=2$.

6. The method of Claim 1, characterized in that the amide compounds have the following structure:

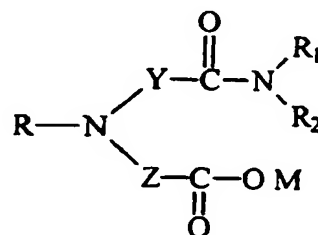


wherein l , m , and n are as defined in the claim 5,

Y is a connecting group selected from alkylene, and the groups Y can be different when $n = 2$, the groups R can be different when $l = 2$, and the groups CONR_1R_2 may be mutually different when $n=2$,

and R , R_1 , and R_2 are as defined above.

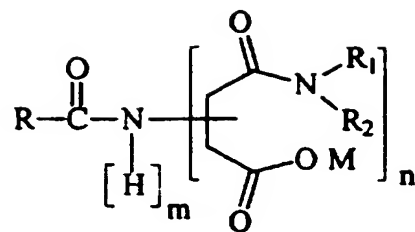
7. The method of Claim 1, characterized in that the amphiphilic compounds have the following structure:



wherein R , R_1 , R_2 , Y , M , l , m , and n are as defined above,

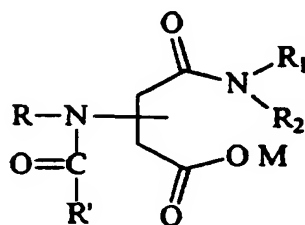
and Z is a connecting group selected from the group alkylene.

8. The method of Claim 1, characterized in that the amide compounds have the following structure:



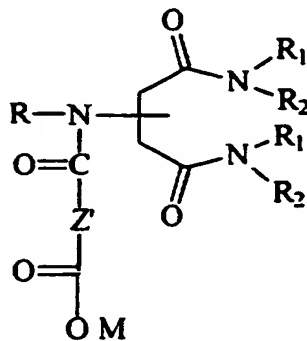
wherein m , n , M , R , R_1 , R_2 are as defined above, and further, the first R_1 and R_2 may be different from the second R_1 and R_2 when $n=2$.

9. The method of Claim 1, characterized in that the amide compounds have the following structure:



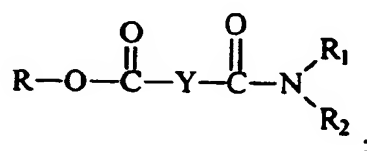
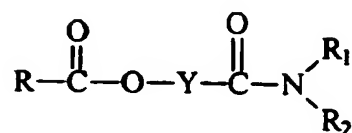
where R is a linear or branched, alkyl or alkenyl group having 6 - 24 carbons atoms, R' is a linear or branched, alkyl or alkenyl group having 1 - 24 carbons atoms, and M , R_1 , and R_2 have the meanings defined above.

10. The method of Claim 1, characterized in that the amide compounds have the following structure:



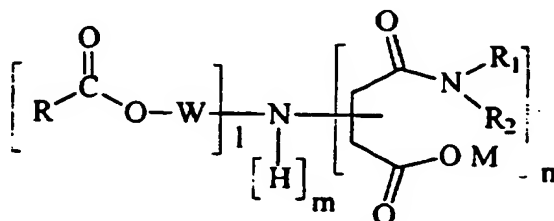
wherein M, R, R₁, and R₂ have the meanings defined above, and Z' is a connecting group selected from the group alkylene.

11. The method of Claim 1, characterized in that the amide compounds have the following structure:



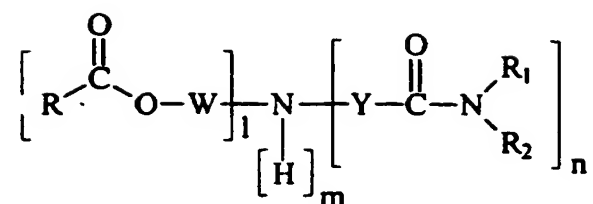
wherein R, R₁, R₂, and Y are as defined above.

12. The method of Claim 1, characterized in that the amide compounds have the following structure:



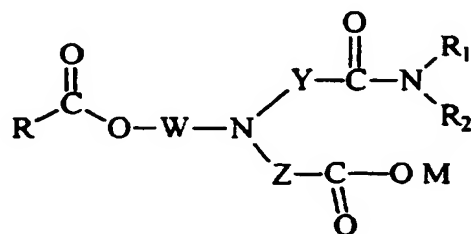
where W is a connecting group selected from alkylene, alkyleneoxy and polyalkyleneoxy, and R, R₁, R₂, M, l, m, and n are as defined above, whereby the first R and W can be different from the second R and W when l=2, and further the first R₁ and R₂ may be different from the second R₁ and R₂ when n=2.

13. The method of Claim 1, characterized in that the amide compounds have the following structure:



where W, R, R₁, R₂, Y, l, m, and n are as defined above, whereby the first R and W can be different from the second R and W when l=2, and further the first R₁ and R₂ may be different from the second R₁ and R₂ when n=2.

14. The method of Claim 1, characterized in that the amide compounds have the following structure:



wherein W, Y, M, R, R₁, and R₂ have the meanings defined above, and Z is a connecting group selected from the group alkylene.

15. The method according to one or more of claims 1-14, characterized in that between 0.05 and 10 wt. %, based on the water content, of the additive is added to the water/hydrocarbon mixture.
16. The method according to one or more of claims 1-15, characterized in that between 0.1 and 0.8 wt. %, based on the water content, of the additive is added to the water/hydrocarbon mixture.
17. The method according to one or more of claims 1-14, characterized in that a corrosion inhibitor is added to the water/hydrocarbon mixture.

18. The method according to one or more of claims 1-17, characterized in that a polymer of an ethylenically unsaturated N-heterocyclic carbonyl compound is added to the hydrocarbon water mixture.
19. The method according to claim 18, characterized in that the polymer is a polymer or copolymer of vinyl caprolactam or vinyl pyrrolidone.
20. The method of one of more of claim 18, characterized in that a N-alkyl or N,N-dialkyl acrylamide polymer is added to the hydrocarbon/water mixture.
21. The method according to claim 18, characterized in that the polymer is a polymer or copolymer of acryloylpyrrolidine or N-isopropylacrylamide.
22. The method according to one or more of claims 1-16, characterized in that a polymer with a heteroatom backbone and sidechains containing amide groups is added to the hydrocarbon water mixture.
23. The method according to one or more of claims 18-22, characterized in that the polymer is a copolymer derived from a comonomer with 6-30 carbon atoms.
24. The method according to claim 23, characterized in that the comonomer is an alkyl acrylate or a unsaturated hydrocarbon.
25. The method according to claims 1-24, characterized in that a salt is also added to the hydrocarbon/water mixture.

26. The method according to claim 25, characterized in that the salt is sodium chloride.
27. The method according to claims 1-26, characterized in that the products added to the hydrocarbon/water mixture also contain an aromatic, ketone, ester, alcohol or glycol solvent.
28. The method according to claims 1-27, characterized in that R_1 and R_2 are chosen from the groups ethyl, isopropyl, tetramethylene and isobutyl.
29. The method according to claims 1-28, characterized in that one or more second additives is used together with the first additive to reduce the formation and stability of emulsions in the hydrate forming fluids.
30. The method according to claim 29, characterized in that the second additive is an aromatic, ketone, alcohol, glycol or polyglycol.
31. The method according to claim 29, characterized in that the second additive is an ester
32. The method according to claims 29-30, characterized in that the second additive is butyl glycol.
33. The use of the additives described in the preceding claims for the inhibition of gas hydrate formation and agglomeration in oil and gas transport pipelines.



Application No: GB 0011316.7
Claims searched: 1-33

Examiner: Dr Lawrence Cullen
Date of search: 7 September 2000

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.R): C5E (ECN)

Int CI (Ed.7): E21B 37/06

Other: Online: CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	WO 98/23843 A1 (CLARIANT) see page 2, 3 rd paragraph; claims 1, 25-28	1-4, 15-23, 33 at least
A	WO 97/07320 A1 (EXXON) see page 24, lines 10 to page 31, line 5	-
A	WO 96/08672 A1 (EXXON) see claims 1, 8 and 14; see structures pages 13-16.	-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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